

**Pigment containing varnish for writing systems.**

Patent Number: EP0254187  
Publication date: 1988-01-27  
Inventor(s): GROSSMANN ALEXANDER DIPL-ING F; MELNITZKI ARTHUR  
Applicant(s): HUBER FA MICHAEL MUENCHEN (DE); SIEMENS AG (DE)  
Requested Patent: ☐ EP0254187, A3  
Application Number: EP19870110164 19870714  
Priority Number(s): DE19863624587 19860721  
IPC Classification: C09D11/00  
EC Classification: C09D11/00C6, C09D11/16B  
Equivalents:  
Cited patent(s): US4228438; US4680058; FR2537987

---

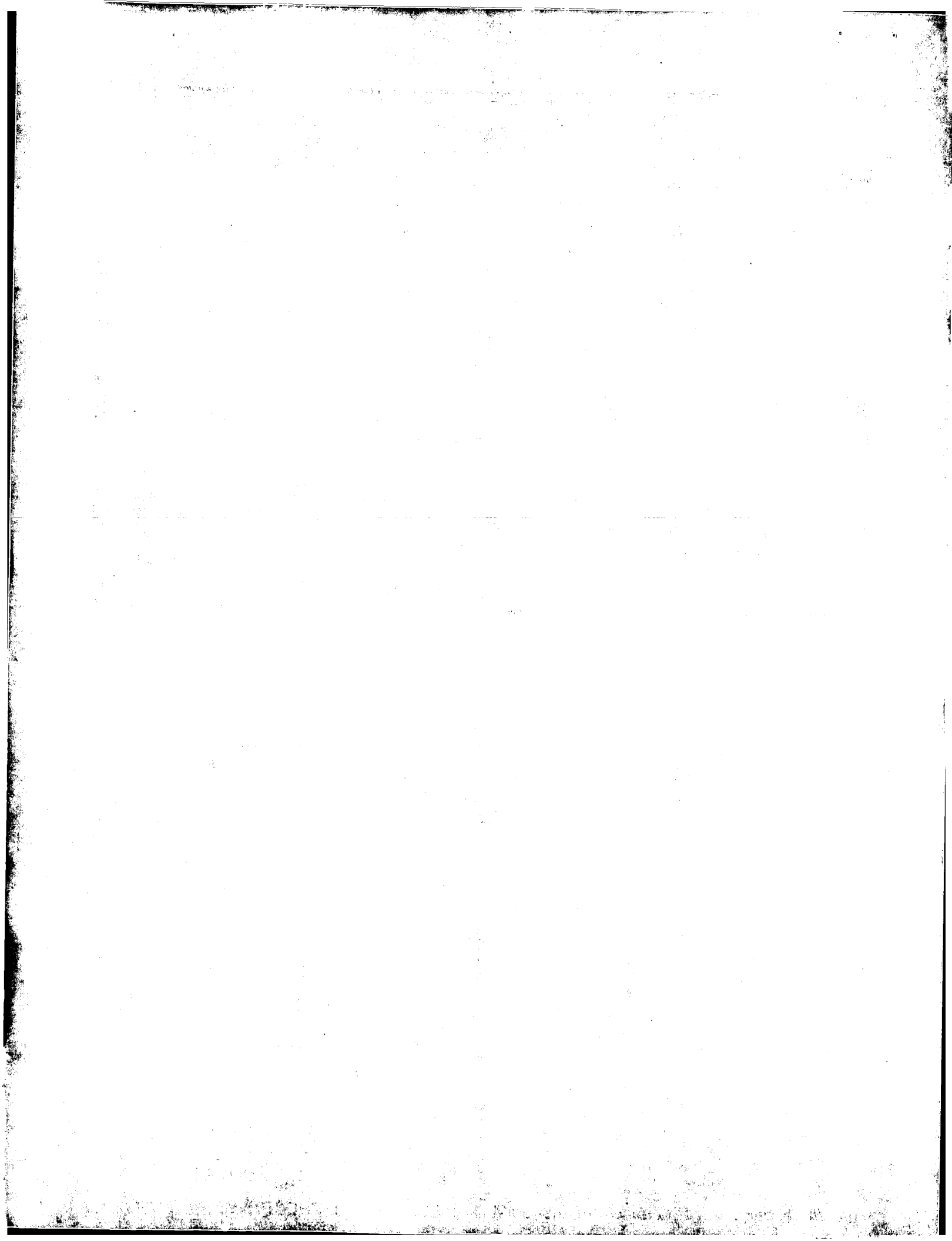
**Abstract**

---

The pigmented, preferably white, lacquer, which is processible in ink-jet writing systems, contains special surface-treated white pigments, for example rutile, which have been treated with a dispersing and antissettling agent in order to prevent the pigments from settling out within the writing head or in the storage vessel within a limited use period (for example one week). The mixture also contains radical polymerisable monomers, glycols or derivatives thereof as solvent, and surface-active substances.

---

Data supplied from the esp@cenet database - I2



(19)



Europäisches Patentamt  
European Patent Office  
Office européen des brevets

(11) Veröffentlichungsnummer:

**0 254 187**  
**A2**

(12)

## EUROPÄISCHE PATENTANMELDUNG

(21) Anmeldenummer: 87110164.8

(51) Int. Cl. 4: C09D 11/00

(22) Anmeldetag: 14.07.87

(30) Priorität: 21.07.86 DE 3624587

(43) Veröffentlichungstag der Anmeldung:  
27.01.88 Patentblatt 88/04(84) Benannte Vertragsstaaten:  
CH DE ES FR GB IT LI NL SE

(71) Anmelder: Siemens Aktiengesellschaft Berlin  
und München  
Wittelsbacherplatz 2  
D-8000 München 2(DE)

Anmelder: MICHAEL HUBER MÜNCHEN GMBH  
Feldkirchener Strasse 15  
D-8011 Kirchheim-Heimstetten(DE)

(72) Erfinder: Melnitzki, Arthur  
Münchbergstrasse-7a  
D-8000 München 90(DE)  
Erfinder: Grossmann, Alexander, Dipl.-Ing. FH  
Gebelestrasse 22  
D-8000 München 80(DE)

(74) Vertreter: Mehl, Ernst, Dipl.-Ing. et al  
Postfach 22 01 76  
D-8000 München 22(DE)

(54) Pigmentierter Lack für Schreibsysteme.

(57) Zur Beschriftung von dunklem Untergrund von Kunststoff-bzw. Metalloberflächen dient ein pigmentierter, vorzugsweise weißer Lack, der in Ink-Jet-Schreibsystemen verarbeitbar ist. Damit sich die Pigmente im Schreibkopf oder im Vorratsbehälter innerhalb einer begrenzten Einsatzdauer (zum Beispiel eine Woche) nicht festsetzen, sind spezielle oberflächenbehandelte Weißpigmente, zum Beispiel Rutil, mit einem Dispergier- und Antiabsetzmittel versehen. Diesem Gemisch sind ferner radikalisch polymerisierbare Monomere zugesetzt und als Lösungsmittel Glykole oder Derivate und oberflächenaktive Substanzen beigegeben.

EP 0 254 187 A2

### Pigmentierter Lack für Schreibsysteme.

Die Erfindung betrifft pigmentierten, hellen, vorzugsweise weißen Lack für Schreibsysteme, insbesondere Ink-Jet-Schreibsysteme, zur Beschriftung auf dunklem Untergrund zum Beispiel in Form von Kunststoff- bzw. Metalloberflächen.

Das der Erfindung zugrundeliegende Problem besteht in der Hauptsache darin, eine genügende Menge Farbpigmente in einer Flüssigkeit so zu suspendieren, daß sich die Pigmente weder im Schreibkopf noch im Vorratsbehälter über eine Einsatzdauer von zum Beispiel einer Woche absetzen. Zur Erreichung einer ausreichenden Deckkraft müssen ca. 5 .. 20 % Massenanteil Pigmente suspendiert werden.

Das Problem ist bisher ungelöst, da auch schon bei kurzer Nichtbenutzung des Schreibsystems sich bei der Verwendung bekannter Lacke die Pigmente absetzen und die Düsen verstopfen. Auch bei der Verwendung von heller Farbe, zum Beispiel gelb als Mischung von Weißpigment und einem gelben, organischen Farbpigment, konnte nicht verhindert werden, daß sich die Pigmente bereits nach kurzer Zeit im Schreibkopf und im Vorratsbehälter absetzen.

Der Erfindung liegt die Aufgabe zugrunde, den eingangs erwähnten pigmentierten Lack herzustellen. Dieser Lack soll auf nahezu allen Kunststoffoberflächen, wie zum Beispiel Polyester, Polyimid, Polyethylen, Polystyrol, Polysulfon, ABS, PVC, gut haften und innerhalb von 30 bis 60 Sekunden bei Raumtemperatur trocknen. Das gleiche gilt für metallische Oberflächen.

Die der Erfindung zugrundeliegende Aufgabe wird gemäß den kennzeichnenden Merkmalen der Patentansprüche gelöst. Unter oberflächenbehandelten Titandioxid versteht man eine spezielle Behandlung mit siliziumorganischen Verbindungen.

Das oberflächenbehandelte Titandioxid-Pigment wird in einer Korngröße von zum Beispiel  $< 5 \mu\text{m}$  verwendet. Als Dispergier- und Antiabsetzmittel eignen sich zum Beispiel modifiziertes Ricinusöl und sogenannte pyrogene Kieselsäure in einem Konzentrationsbereich von 0 ... 5 %.

Um die Haftung auf der Oberfläche zu gewährleisten, werden radikalisch polymerisierbare Monomere wie Acrylate, Styrol, Divinylbenzol, Vinylacetat in einer Konzentration von 1 ... 15 % zugesetzt.

Zur Einstellung der Oberflächenspannung und der Viskosität werden als Lösungsmittel Glykole, zum Beispiel Ethyl-, Butylglykol oder deren Derivate, zum Beispiel Ethylglykolacetat, zugemischt. Ihr Anteil liegt zwischen 45 .. 90 %. Weiterhin

kommen in Frage Alkohole von Ethanol bis Hexanol. Als oberflächenaktive Substanzen eignen sich zum Beispiel Titansäureester in einem Bereich von 0 ... 0,5 %.

Der Lack nach der Erfindung erfüllt folgende Abnahmwerte:

Viskosität:  $24 \pm 1$  s im Auslaufbecher 3 mm in Anlehnung an DIN 53211,

Oberflächenspannung:  $29 \pm 0,5$  m N/m.

Mit dem Lack nach der Erfindung werden folgende Eigenschaften erreicht: Die Beschriftung ist beständig gegen Kratzen mit dem Fingernagel. Die Beschriftung von Kabeln ist zum Beispiel auf PVC in Gegenwart von Öl, Benzin, 10 %ig Waschmittellösung bei einer Belastung von 500 gr abriebbeständig.

#### Ausführungsbeispiel:

Der Lack besteht aus folgenden Komponenten (Massenanteil):

5 ... 20  $\text{TiO}_2$  (Rutil), oberflächenbehandelt  
1 ... 15 lösliches Acrylat

0 ... 5 Dispergier- und Antiabsetzmittel

45 ... 90 Glykole und deren Derivate

0 ... 5 Oberflächenaktive Substanzen

#### Ansprüche

1. Pigmentierter heller, vorzugsweise weißer Lack für Schreibsysteme, insbesondere Ink-Jet-Schreibsysteme, zur Beschriftung auf dunklem Untergrund, zum Beispiel auf Kunststoff- bzw. Metalloberflächen, dadurch gekennzeichnet, daß oberflächenbehandelte Farbpigmente (vorzugsweise weiße Farbpigmente) mit einem Dispergier- und Antiabsetzmittel versehen werden, radikalisch polymerisierbare Monomere zugesetzt und als Lösungsmittel Glykole oder deren Derivate und oberflächenaktive Substanzen zusammengemischt werden.

2. Lack nach Anspruch 1, dadurch gekennzeichnet, daß als oberflächenbehandelte Weißpigmente zum Beispiel Titandioxid (Rutil), Magnesiumoxid oder Bariumsulfat in einer Korngröße  $< 5 \mu\text{m}$  verwendet werden.

3. Lack nach Anspruch 1, dadurch gekennzeichnet, daß als Dispergier- und Antiabsetzmittel zum Beispiel modifiziertes Rizinusöl und oder pyrogene Kieselsäure verwendet werden.

4. Lack nach Anspruch 1, **dadurch gekennzeichnet**, daß als radikalisch polymerisierbare Monomere Acrylate, Styrol, Divinylbenzol, oder Vinylazetat zugesetzt werden.

5. Lack nach Anspruch 1, **dadurch gekennzeichnet**, daß als Lösungsmittel zum Beispiel Äthyl-, Butylglykol oder Ethylglykolazetat bzw. Alkohole von Ethanol bis Hexanol zugemischt wird.

6. Lack nach Anspruch 1, **dadurch gekennzeichnet**, daß als oberflächenaktive Substanzen zum Beispiel Titansäureester verwendet wird.

7. Lack nach Anspruch 1, **dadurch gekennzeichnet**, daß die einzelnen Komponenten in folgenden Massenanteilen zusammengemischt werden:

5 ... 20 TiO<sub>2</sub> Rutil, oberflächenbehandelt

1 ... 15 lösliches Acrylat

0 ... 5 Dispergier- und Antiabsetzmittel

45 ... 90 Glykole und deren Derivate

0 ... 5 oberflächenaktive Substanzen.

5

10

15

25

30

35

40

45

50

55



①② **EUROPÄISCHE PATENTANMELDUNG**

②① Anmeldenummer: 87110164.8

⑤① Int. Cl.4: **C09D 11/00**

②② Anmeldetag: 14.07.87

③③ Priorität: 21.07.86 DE 3624587

④③ Veröffentlichungstag der Anmeldung:  
27.01.88 Patentblatt 88/04

⑧④ Benannte Vertragsstaaten:  
CH DE ES FR GB IT LI NL SE

⑥⑧ Veröffentlichungstag des später veröffentlichten  
Recherchenberichts: 26.07.89 Patentblatt 89/30

⑦① Anmelder: Siemens Aktiengesellschaft Berlin  
und München  
Wittelsbacherplatz 2  
D-8000 München 2(DE)

Anmelder: MICHAEL HUBER MÜNCHEN GMBH  
Feldkirchener Strasse 15  
D-8011 Kirchheim-Heimstetten(DE)

⑦② Erfinder: Melnitzki, Arthur  
Münchbergstrasse 7a  
D-8000 München 90(DE)  
Erfinder: Grossmann, Alexander, Dipl.-Ing. FH  
Gebelestrasse 22  
D-8000 München 80(DE)

⑦④ Vertreter: Mehl, Ernst, Dipl.-Ing. et al  
Postfach 22 13 17  
D-8000 München 22(DE)

⑤④ **Pigmentierter Lack für Schreibsysteme.**

⑤⑦ Zur Beschriftung von dunklem Untergrund von Kunststoff- bzw. Metalloberflächen dient ein pigmentierter, vorzugsweise weißer Lack, der in Ink-Jet-Schreibsystemen verarbeitbar ist. Damit sich die Pigmente im Schreibkopf oder im Vorratsbehälter innerhalb einer begrenzten Einsatzdauer (zum Beispiel eine Woche) nicht festsetzen, sind spezielle oberflächenbehandelte Weißpigmente, zum Beispiel Rutil, mit einem Dispergier- und Antiabsetzmittel versehen. Diesem Gemisch sind ferner radikalisch polymerisierbare Monomere zugesetzt und als Lösungsmittel Glykole oder Derivate und oberflächenaktive Substanzen beigegeben.

EP 0 254 187 A3



Europäisches  
Patentamt

# EUROPÄISCHER RECHERCHENBERICHT

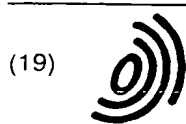
Nummer der Anmeldung

EP 87 11 0164

EINSCHLÄGIGE DOKUMENTE			
Kategorie	Kennzeichnung des Dokuments mit Angabe, soweit erforderlich, der maßgeblichen Teile	Betrifft Anspruch	KLASSIFIKATION DER ANMELDUNG (Int. Cl.4)
A	US-A-4 228 438 (BELL TELEPHONE) ----		C 09 D 11/00
A	US-A-4 680 058 (HITACHI) ----		
A	FR-A-2 537 987 (PILOT INK.) -----		
			RECHERCHIERTE SACHGEBIETE (Int. Cl.4)
			C 09 D
Der vorliegende Recherchenbericht wurde für alle Patentansprüche erstellt			
Recherchenort DEN HAAG		Abschlußdatum der Recherche 27-04-1989	Prüfer BUSCAGLIONE Y.
KATEGORIE DER GENANNTEN DOKUMENTE X : von besonderer Bedeutung allein betrachtet Y : von besonderer Bedeutung in Verbindung mit einer anderen Veröffentlichung derselben Kategorie A : technologischer Hintergrund O : mündliche Offenbarung P : Zwischenliteratur		T : der Erfindung zugrunde liegende Theorien oder Grundsätze E : älteres Patentdokument, das jedoch erst am oder nach dem Anmeldedatum veröffentlicht worden ist D : in der Anmeldung angeführtes Dokument L : aus andern Gründen angeführtes Dokument & : Mitglied der gleichen Patentfamilie, übereinstimmendes Dokument	

EPO FORM 1503 03.82 (P0403)





Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11) **EP 1 036 831 A1**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:  
20.09.2000 Bulletin 2000/38

(51) Int Cl.7: **C09D 11/00**

(21) Application number: 00302099.7

(22) Date of filing: 15.03.2000

(84) Designated Contracting States:  
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU  
MC NL PT SE**  
Designated Extension States:  
**AL LT LV MK RO SI**

(30) Priority: 16.03.1999 JP 6972899  
24.03.1999 JP 8047099

(71) Applicant: **SEIKO EPSON CORPORATION**  
Shinjuku-ku Tokyo-to (JP)

(72) Inventors:  
• **Tanabe, Seiichi**, c/o Seiko Epson Corporation  
Suwa-shi, Nagano-ken (JP)  
• **Takemoto, Kiyohiko**,  
c/o Seiko Epson Corporation  
Suwa-shi, Nagano-ken (JP)

(74) Representative: **Kyle, Diana**  
Elkington and Fife  
Prospect House  
8 Pembroke Road  
Sevenoaks, Kent TN13 1XR (GB)

(54) **Photocurable ink composition for ink jet recording and ink jet recording method using the same**

(57) Disclosed is a photocurable ink composition for use in an ink jet recording method wherein an ink composition is brought into contact with a recording medium followed by a photocuring reaction to perform printing. The photocurable ink composition can offer good coating strength, chemical resistance, dispersion stability,

and printing stability. This photocurable ink composition comprises at least a colorant, a urethane oligomer, a monomer having a tri- or higher functional reactive group, a photopolymerization initiator, and an aqueous solvent. After printing the photocurable ink composition; ultraviolet light is applied to cure the print. The colorant is preferably anatase titanium dioxide.

EP 1 036 831 A1

## Description

BACKGROUND OF THE INVENTION5 Field of the Invention

[0001] The present invention relates to an ink composition for ink jet recording, and an ink jet recording method using the same.

10 Background Art

[0002] Ink jet recording is a printing method wherein droplets of an ink composition are ejected and deposited onto a recording medium, such as paper, to conduct printing. This ink jet recording method has a feature that images having high resolution and high quality can be printed at a high speed. In general, the ink composition used in the ink jet recording comprises an aqueous solvent as a main component and, added thereto, a colorant component and a wetting agent, such as glycerin, for preventing clogging.

[0003] A component, capable of stably fixing a colorant onto a recording media, into the ink composition is required for printing of the water-base ink composition on papers, cloths and other recording media which are less likely to be penetrable by the ink composition, and plates, films and other recording media produced from metals, plastics and other materials, which are not penetrable by the ink composition, for example, phenol, melamine, vinyl chloride, acryl, and polycarbonate resins. In particular, in the case of printing, for example, on printed wiring boards, rapid drying and good chemical resistance are required of the ink composition.

[0004] In order to meet this requirement, an ink composition has been proposed which contains a component of which the molecular weight is increased upon ultraviolet irradiation (for example, Japanese Patent Laid-Open No. 216379/1991). An ultraviolet-curable ink composition comprising a colorant, an ultraviolet-curable material, a photopolymerization initiator and the like has also been proposed (for example, U.S. Patent No. 5,623,001). The claimed advantage of these ink compositions and ink jet recording methods using the same is to yield images having improved quality through the prevention of feathering or bleeding of the ink composition on recording media.

[0005] In an ink jet recording method using the ink composition containing a component, of which the molecular weight is increased upon ultraviolet irradiation, the ink composition is deposited on a recording medium followed by ultraviolet irradiation. Upon ultraviolet irradiation, the photopolymerization initiator contained in the ink composition produces radicals or the like which induce polymerization of an oligomer and a monomer contained in the ink composition. This results in curing of the ink composition, permitting the colorant contained in the ink composition to be fixed onto the recording medium. The fixation of the colorant is considered to realize prints which have high coating strength, solvent resistance, and color density and, at the same time, have no significant feathering or bleeding and unevenness. This type of ink composition for ink jet recording is sometimes called a "photocurable ink composition for ink jet recording."

[0006] Further, for the prevention of a dye as a colorant from being separated, the improvement of scratch/rubbing resistance and printing reliability, the prevention of feathering or bleeding after printing, the enhancement of drying properties of the ink and other purposes, disclosed are an ink for ink jet recording, comprising two liquids, an ink composition containing a colorant and a reaction solution containing a polymerization initiator, and an ink jet recording method wherein printing is carried out using these two liquids on recording media (for example, Japanese Patent Laid-Open Nos. 186725/1993 and 218018/1996).

[0007] According to the ink for ink jet recording, comprising two liquids, one of the ink composition and the reaction solution contains a photopolymerization initiator or a photocurable resin. The claimed advantage of using two divided liquids, that is, the ink composition and the reaction solution, is to suppress a dark reaction to enable the storage of the ink composition and the reaction solution for a long period of time and, in addition, to realize prints having excellent lightfastness and heat resistance.

[0008] On the other hand, ink jet recording, which involves the formation of a white print on a recording medium, uses an ink composition containing a white pigment as a colorant component. White pigments used in this method include white inorganic pigments, such as oxides, sulfides, sulfates, carbonates and the like of zinc, lead, barium, titanium, and antimony. Titanium oxide is known as a white pigment possessing excellent covering power, coloring power, and chemical resistance.

[0009] Further, a nonaqueous white pigment ink composition containing a colorant having a specific particle diameter has been proposed (for example, Japanese Patent Publication No. 45663/1990). The claimed advantage of this ink composition is to realize good dispersibility of the ink composition and good printing stability and to prevent clogging of the recording head in the ink jet recording apparatus, by virtue of the specific particle diameter of the white pigment.

SUMMARY OF THE INVENTION

[0010] The present inventors have now found that, in a photocurable ink composition for ink jet recording, the use of a urethane oligomer and a monomer having a tri- or higher functional reactive group can significantly improve coating strength, chemical resistance, dispersion stability, and printing stability. The present inventors have further found that, in the white ink composition for ink jet recording, anatase titanium dioxide, when used as the colorant, can improve the dispersion stability and printing stability of the ink composition. The present inventors have further found that the use of anatase titanium dioxide, a photopolymerization initiator, an oligomer, and a monomer in the photocurable ink composition for ink jet recording can significantly improve, in addition to dispersion stability and printing stability, polymerization efficiency and coating strength. The present invention has been made based on such finding.

[0011] Accordingly, it is an object of the present invention to provide an ink composition for ink jet recording, capable of realizing good ink jet recording and good images, and to provide an ink jet recording method using this ink composition.

[0012] According to a first aspect of the present invention, there is provided a photocurable ink composition for ink jet recording, comprising at least a colorant, a urethane oligomer, a monomer having a tri- or higher functional reactive group, a photopolymerization initiator, and an aqueous solvent.

[0013] According to a second aspect of the present invention, there is provided a white ink composition for ink jet recording, comprising at least anatase titanium dioxide and an aqueous solvent.

[0014] According to a third aspect of the present invention, there is provided a photocurable white ink composition for ink jet recording, comprising at least anatase titanium dioxide, a photopolymerization initiator, an oligomer, a monomer, and an aqueous solvent.

DESCRIPTION OF THE PREFERRED EMBODIMENTS Ink composition according to first aspect of invention

[0015] The photocurable ink composition for ink jet recording according to the first aspect of the present invention comprises at least a colorant, a urethane oligomer, a monomer having a tri- or higher functional reactive group, a photopolymerization initiator, and an aqueous solvent. The ink composition according to the first aspect of the present invention has high storage stability, can realize stable printing in ink jet recording, and can yield images having excellent coating strength and chemical resistance. The reason why this advantage can be obtained has not been fully elucidated yet, the reason is believed to reside in that the urethane oligomer has high compatibility with the monomer having a tri- or higher functional reactive group and can stably dissolve or disperse other ingredients constituting the ink composition.

Urethane oligomer

[0016] The ink composition according to the first aspect of the present invention contains a urethane oligomer. The urethane oligomer according to the present invention refers to an oligomer having in its molecule at least one urethane bond and at least one radically polymerizable unsaturated double bond. The oligomer refers to a molecule with a medium relative molecular mass (having the same meaning as molecular weight) which has a structure constituted by repetition of units obtained substantially or conceptually from molecules having a low relative molecular mass a small number of times, generally about 2 to 20 times. Further, the oligomer used in the present invention is called "photopolymerizable prepolymer," "base resin," or "acrylic oligomer."

[0017] The urethane oligomer according to the present invention has one to several acryloyl groups as the functional group and thus causes a polymerization reaction with the monomer or the like upon ultraviolet irradiation or the like to form a crosslinked polymer.

[0018] Urethane oligomers usable in the present invention include oligomers produced by an addition reaction of a polyol with a polyisocyanate and a polyhydroxy compound and, in addition, those which may be classified, according to molecular structure constituting the skeleton, into polyester urethane acrylates, polyether urethane acrylates, polybutadiene urethane acrylates, and polyol urethane acrylates.

[0019] The urethane oligomer according to the present invention generally has a molecular weight of about 500 to 20,000, preferably about 500 to 10,000.

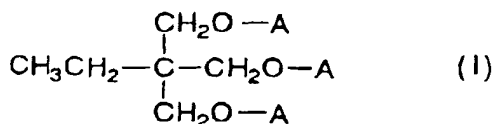
[0020] The content of the urethane oligomer in the ink composition according to the present invention is generally about 1 to 50% by weight, preferably about 3 to 30% by weight.

Monomer

[0021] The ink composition according to the first aspect of the present invention contains a monomer having a tri- or higher functional reactive group. The monomer having a tri- or higher functional reactive group according to the

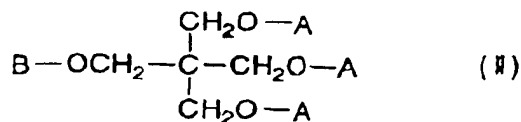
present invention refers to a monomer having in its basic structure three or more radically polymerizable unsaturated double bonds, preferably acryloyl groups. The term "monomer" used herein refers to a molecule which can constitute constituent units of the basic structure of a polymer. The monomer according to the present invention is also called a "photopolymerizable monomer," and examples thereof include tri- or higher functional polyfunctional acrylates.

[0022] According to a preferred embodiment of the present invention, the monomer having a tri- or higher functional reactive group is an acrylate monomer which has trimethylolpropane represented by formula (I), pentaerythritol represented by formula (II), or dipentaerythritol represented by formula (III) as a basic structure and at least three acryloyl groups:



wherein

A represents  $\text{CH}_2=\text{CHC}(\text{O})$  or  $\text{CH}_2=\text{CHC}(\text{O})\text{R}_n$  wherein R represents a straight-chain or branched alkoxy group having 1 to 5 carbon atoms, preferably an ethoxy or propoxy group, and n represents the number of repetitions of R and is 1 to 10,

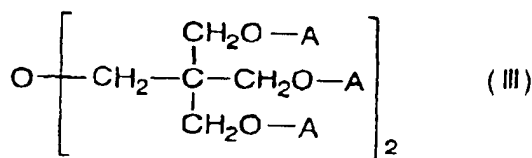


wherein

A represents H,  $\text{CH}_2-\text{CHC}(\text{O})$ , or  $\text{CH}_2=\text{CHC}(\text{O})\text{R}_n$  wherein R represents a straight-chain or branched alkoxy group having 1 to 5 carbon atoms, preferably an ethoxy or propoxy group, and n represents the number of repetitions of R and is 1 to 10 and

B represents H,  $\text{CH}_2=\text{CHCO}$ , or a higher acyl group having 1 to 5 carbon atoms,

provided that at least three out of all substituents of A and B comprise an acryloyl group; and



wherein

A represents H,  $\text{CH}_2=\text{CHC}(\text{O})$ , or  $\text{CH}_2=\text{CHC}(\text{O})\text{R}_n$  wherein R represents a straight-chain or branched alkoxy group having 1 to 5 carbon atoms, preferably an ethoxy or propoxy group, or a lactone having 1 to 5 carbon atoms, preferably  $\epsilon$ -caprolactone, and n represents the number of repetitions of R and is 1 to 10, and B represents H,  $\text{CH}_2=\text{CHCO}$ , or a higher acyl group having 1 to 5 carbon atoms,

provided that at least three out of all substituents of A comprise an acryloyl group.

[0023] The monomer in the ink composition according to the first aspect of the present invention has a structure of an acrylate of a low-molecular polyol and advantageously cures rapidly.

[0024] Specific examples of monomers usable in the ink composition according to the first aspect of the present invention include glyceryl triacrylate, trimethylolpropane triacrylate, pentaerythritol triacrylate, dipentaerythritol hexaacrylate, dipentaerythritol polyacrylate (those having 3 or more acryloyl groups), and isocyanurate triacrylate. Among

them, dipentaerythritol polyacrylate and dipentaerythritol polyacrylate (those having 3 or more acryloyl groups) are preferred.

[0025] According to the present invention, the molecular weight of the monomer is generally about 200 to 3,000, preferably about 300 to 2,000.

[0026] The content of the monomer in the ink composition according to the first aspect of the present invention is about 1 to 50% by weight, preferably about 3 to 30% by weight.

[0027] The oligomer is copolymerized with a monomer to form a three-dimensional structure. Therefore, the content of the oligomer or the monomer in the ink composition according to the present invention should be determined by taking into consideration the polymerization efficiency, the polymerization speed, the resistance to shrinkage after polymerization, the polymer coating strength and the like. Specifically, in the ink composition according to the present invention, the content ratio of the urethane oligomer to the monomer having a tri- or higher functional reactive group is approximately in the range of 95 : 5 to 40 : 60, preferably approximately in the range of 90 : 10 to 50 : 50.

#### Photopolymerization initiator

[0028] The ink composition according to the first aspect of the present invention contains a photopolymerization initiator. The photopolymerization initiator absorbs, for example, ultraviolet light with wavelengths of about 250 to 450 nm to produce radicals or ions which initiate the polymerization of the oligomer and the monomer.

[0029] Representative examples of photopolymerization initiators usable in the present invention include benzoin methyl ether, benzoin ethyl ether, isopropyl benzoin ether, isobutyl benzoin ether, 1-phenyl-1,2-propanedione-2-(o-ethoxycarbonyl)oxime, benzyl, diethoxyacetophenone, benzophenone, chlorothioxanthone, 2-chlorothioxanthone, isopropylthioxanthone, 2-methylthioxanthone, polyphenyl polychloride, and hexachlorobenzene. Among them, isobutyl benzoin ether and 1-phenyl-1,2-propanedione-2-(o-ethoxycarbonyl)oxime are preferred.

[0030] Commercially available photopolymerization initiators under tradename designations of Vicure 10, 30 (manufactured by Stauffer Chemical), Irgacure 184, 651, 2959, 907, 369, 1700, 1800, 1850, 819 (manufactured by Ciba Specialty Chemicals, K.K.), Darocure 1173 (manufactured by EM Chemical), Quantacure CTx, ITX (manufactured by Aceto Chemical), and Lucirin TPO (manufactured by BASF) may also be used.

#### Colorant

[0031] The colorant contained in the ink composition according to the first aspect of the present invention may be a pigment dispersible in water and/or a dye dispersible in water.

[0032] The pigment may be either an inorganic pigment or an organic pigment. Inorganic pigments usable herein include, in addition to titanium oxide and iron oxide, carbon blacks produced by known processes, such as contact, furnace, and thermal processes.

[0033] Organic pigments usable herein include azo pigments (including azo lake, insoluble azo pigment, condensed azo pigment, and chelate azo pigment), polycyclic pigments (for example, phthalocyanine, perylene, perinone, anthraquinone, quinacridone, dioxazine, thioindigo, isoindolinone, and quinophthalone pigments), dye chelates (for example, basic dye chelates and acid dye chelates), nitro pigments, nitroso pigments, and aniline black.

[0034] Dyes usable herein include dispersible dyes usable for ink jet recording.

[0035] According to a preferred embodiment of the present invention, the colorant is preferably anatase titanium dioxide. The ink composition containing anatase titanium dioxide has an advantage over the ink composition containing titanium dioxide having other crystal structures, such as rutile titanium dioxide and brookite titanium dioxide, in that the dispersion stability of the ink composition can be improved. Further, the ink composition containing anatase titanium dioxide according to the present invention, when used in ink jet recording, can realize stable printing and good images.

[0036] The particle diameter of the anatase titanium dioxide as the colorant is preferably about not more than 2.0  $\mu\text{m}$ , particularly preferably not more than 0.2  $\mu\text{m}$ . The anatase titanium dioxide having particle diameters falling within the above range can be considered to improve the dispersibility of the ink composition.

[0037] The term "particle diameter" used herein means 50% particle diameter in terms of volume. The "50% particle diameter in terms of volume" refers to such a diameter that, for the particle size distribution of a population of a titanium dioxide powder, corresponds to 50% of a cumulative curve on particle diameter prepared with the total volume of a population of the titanium dioxide powder being presumed to be 100%.

[0038] The amount of the colorant added to the ink composition according to the present invention is preferably 1 to 50% by weight, more preferably about 2 to 30% by weight.

[0039] According to the ink composition of the present invention, if necessary, two or more dyes and/or pigments may be used as the colorant.

[0040] According to a preferred embodiment of the present invention, the colorant is added, to the ink composition, as a colorant dispersion prepared by dispersing a colorant in an aqueous medium with the aid of a dispersant or a

surfactant. Preferred dispersants usable herein include dispersants commonly used in the preparation of colorant dispersions, for example, polymeric dispersants. It will be apparent to a person having ordinary skill in the art that the dispersant and the surfactant contained in the colorant dispersion serves also as the dispersant and the surfactant in the ink composition.

#### Aqueous solvent and other ingredients

[0041] According to the ink composition of the present invention, the aqueous solvent preferably comprises water and a water-soluble organic solvent. Water may be pure water obtained by ion exchange, ultrafiltration, reverse osmosis, distillation or the like, or ultrapure water. Further, water, which has been sterilized by ultraviolet irradiation or by addition of hydrogen peroxide or the like, is suitable because, when the ink composition is stored for a long period of time, it can prevent the growth of mold or bacteria.

[0042] The water-soluble organic solvent is preferably a low-boiling organic solvent, and specific examples thereof include methanol, ethanol, n-propyl alcohol, iso-propyl alcohol, n-butanol, sec-butanol, tert-butanol, iso-butanol, and n-pentanol. Monohydric alcohols are particularly preferred. The low-boiling organic solvent has the effect of shortening the time taken for drying the ink composition. The amount of the low-boiling organic solvent added is preferably in the range of from 0.1 to 10% by weight, more preferably in the range of from 0.5 to 5% by weight, based on the ink composition.

[0043] According to a preferred embodiment of the present invention, the ink composition further contains a wetting agent comprising a high-boiling organic solvent. Specific examples of preferred high-boiling organic solvents usable herein include: polyhydric alcohols, such as ethylene glycol, diethylene glycol, triethylene glycol, polyethylene glycol, polypropylene glycol, propylene glycol, butylene glycol, 1,2,6-hexanetriol, thioglycol, hexylene glycol, glycerin, trimethylolethane, and trimethylolpropane; alkyl ethers of polyhydric alcohols, such as ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol monobutyl ether, triethylene glycol monomethyl ether, triethylene glycol monoethyl ether, and triethylene glycol monobutyl ether; urea; 2-pyrrolidone; N-methyl-2-pyrrolidone; and 1,3-dimethyl-2-imidazolidinone.

[0044] The amount of the wetting agent added is preferably 0.5 to 40% by weight, more preferably 2 to 20% by weight, based on the ink composition.

[0045] According to a preferred embodiment of the present invention, the ink composition further contains a saccharide. Specific examples of saccharide usable herein include monosaccharides, disaccharides, oligosaccharides (including trisaccharides and tetrasaccharides), and other polysaccharides, preferably glucose, mannose, fructose, ribose, xylose, arabinose, galactose, aldonic acid, glucitol, sorbitol, maltose, cellobiose, lactose, sucrose, trehalose, and maltotriose. The term "polysaccharide" used herein means saccharides in the broad sense as including substances which exist widely in the world of nature, such as alginic acid,  $\alpha$ -cyclodextrin, and cellulose. Derivatives of these saccharides usable herein include reducing sugars of the above saccharides (for example, sugar alcohols represented by the general formula  $\text{HOCH}_2(\text{CHOH})_n\text{CH}_2\text{OH}$ , wherein n is an integer of 2 to 5), oxidizing sugars (for example, aldonic acid or uronic acid), amino acids, and thiosugars. Among them, sugar alcohols are particularly preferred, and specific examples thereof include maltitol and sorbitol.

[0046] The content of the saccharide is generally 0.1 to 40% by weight, preferably 0.5 to 30% by weight, based on the ink composition.

[0047] The ink composition of the present invention may contain a surfactant. Specific examples of surfactants usable herein include anionic surfactants (for example, sodium dodecylbenzenesulfonate, sodium laurylate, and an ammonium salt of polyoxyethylene alkyl ether sulfates), nonionic surfactants (for example, polyoxyethylene alkyl ethers, polyoxyethylene alkyl esters, polyoxyethylene sorbitan fatty acid esters, polyoxyethylene alkylphenyl ethers, polyoxyethylenealkylamines, and polyoxyethylenealkylamides). Further, acetylene glycol (OLFINE Y and Surfynol 82, 104, 440, 465, and 485 (all the above products being manufactured by Air Products and Chemicals Inc.)) may also be used. They may be used alone or in combination of two or more.

[0048] If necessary, polyvalent metal salts, polyallylamines or derivatives thereof, resin emulsions, inorganic oxide colloids, wetting agents, pH adjusters, preservatives, antimolds and the like may be added to the ink composition of the present invention.

#### Process for producing ink composition according to first aspect of invention

[0049] The process for producing the ink composition for ink jet recording according to the first aspect of the present invention comprises the steps of: dissolving or dispersing a monomer having a tri- or higher functional reactive group in a urethane oligomer; and then adding a colorant, a photopolymerization initiator, and an aqueous solvent to the solution or the dispersion.

[0050] The ink composition for ink jet recording produced by the production process according to the present invention

has high storage stability, has excellent printing stability at the time of ink jet recording, and can yield prints having excellent coating strength and chemical resistance on recording media.

[0051] In the process for producing the ink composition according to the first aspect of the present invention, a urethane oligomer is first mixed with a monomer having a tri- or higher functional reactive group to prepare a highly compatible dispersion or solution. According to a preferred embodiment of the present invention, the dispersion or the solution may be prepared by slowly dropwise adding the monomer having a tri- or higher functional reactive group to the urethane oligomer while stirring the urethane oligomer.

[0052] After the preparation of the dispersion or solution comprising the urethane oligomer and the monomer having a tri- or higher functional reactive group, a colorant, a photopolymerization initiator, an aqueous solvent, and optional ingredients are added to the dispersion or the solution. According to a preferred embodiment of the present invention, the addition of the above ingredients to the dispersion or the solution is preferably carried out under light (particularly ultraviolet) shielded conditions from the viewpoint of avoiding such a phenomenon that the oligomer and the monomer are polymerized through the action of the photopolymerization initiator.

[0053] A stirrer commonly used in the production of ink compositions may be used in the production process of the ink composition according to the present invention.

#### Ink composition according to second aspect of invention

[0054] The white ink composition for ink jet recording according to the second aspect of the present invention comprises at least anatase titanium dioxide and an aqueous solvent.

#### Titanium dioxide

[0055] The ink composition containing anatase titanium dioxide according to the present invention has an advantage over the ink composition containing titanium dioxide having other crystal structures, such as rutile titanium dioxide and brookite titanium dioxide, in that the resin can be efficiently cured. Further, the ink composition containing anatase titanium dioxide according to the present invention has excellent dispersion stability and, when used in ink jet recording, can advantageously realize stable printing and good images.

[0056] The particle diameter of the anatase titanium dioxide used in the ink composition according to the present invention may be the same as that described above in connection with the ink composition according to the first aspect of the present invention. The preferred particle diameter may also be the same as that described above in connection with the ink composition according to the first aspect of the present invention.

[0057] The amount of the anatase titanium dioxide added to the ink composition is preferably about 1 to 50% by weight, more preferably about 3 to 30% by weight.

[0058] The ink composition according to the second aspect of the present invention contains at least anatase titanium dioxide. The ink composition may further contain other colorants, such as dyes and pigments, and dispersants or surfactants. The other colorants, such as dyes or pigments, and the dispersants or the surfactants may be the same as those described above in connection with the ink composition according to the first aspect of the present invention.

#### Aqueous solvent and other ingredients

[0059] Aqueous solvents and other ingredients usable in the ink composition according to the second aspect of the present invention may be the same as those described above in connection with the ink composition according to the first aspect of the present invention. Preferred aqueous solvents and other ingredients may also be the same as those described above in connection with the ink composition according to the first aspect of the present invention. When the ink composition according to the second aspect of the present invention contains an aqueous solvent and other ingredients, the contents thereof may be the same as those described above in connection with the ink composition according to the first aspect of the present invention.

#### Ink composition according to third aspect of invention

[0060] The photocurable white ink composition for ink jet recording according to the third aspect of the present invention comprises at least anatase titanium dioxide, a photopolymerization initiator, an oligomer, a monomer, and an aqueous solvent.

#### Titanium dioxide

[0061] The ink composition containing anatase titanium dioxide according to the present invention has an advantage

over the ink composition containing titanium dioxide having other crystal structures, such as rutile titanium dioxide and brookite titanium dioxide, in that the resin can be efficiently cured. Further, the ink composition containing anatase titanium dioxide according to the present invention has excellent dispersion stability and, when used in ink jet recording, can advantageously realize stable printing and good images.

[0062] The particle diameter of the anatase titanium dioxide used in the ink composition according to the third aspect of the present invention may be the same as that described above in connection with the ink composition according to the first aspect of the present invention. The preferred particle diameter may also be the same as that described above in connection with the ink composition according to the first aspect of the present invention.

[0063] The amount of the anatase titanium dioxide added to the ink composition is preferably about 1 to 50% by weight, more preferably about 3 to 30% by weight.

[0064] The ink composition according to the third aspect of the present invention contains at least anatase titanium dioxide. The ink composition may further contain other colorants, such as dyes and pigments, and dispersants or surfactants. The other colorants, such as dyes or pigments, and the dispersants or the surfactants may be the same as those described above in connection with the ink composition according to the first aspect of the present invention.

#### Photopolymerization initiator

[0065] The ink composition according to the third aspect of the present invention contains a photopolymerization initiator. The photopolymerization initiator may be the same as that described above in connection with the first aspect of the present invention.

#### Oligomer

[0066] The ink composition according to the third aspect of the present invention contains an oligomer. The oligomer refers to a molecule with a medium relative molecular mass which has a structure constituted by repetition of units obtained substantially or conceptually from molecules having a low relative molecular mass a small number of times, generally about 2 to 20 times. Further, the oligomer used in the present invention is called "photopolymerizable prepolymer," "base resin," or "acrylic oligomer."

[0067] The oligomer according to the third aspect of the present invention has one to several acryloyl groups as the functional group and thus causes a polymerization reaction with the monomer or the like upon ultraviolet irradiation or the like to form a crosslinked polymer.

[0068] Oligomers usable in the third aspect of the present invention may be classified, for example, according to molecular structure constituting the skeleton, into polyester acrylates, polyurethane acrylates, epoxy acrylates, polyether acrylates, oligoacrylates, alkyd acrylates, and polyol acrylates. Among them, polyester acrylates and polyurethane acrylates are preferred with polyurethane acrylates being particularly preferred.

[0069] The molecular weight of the oligomer used in the third aspect of the present invention is generally about 5,000 to 20,000, preferably about 500 to 10,000.

[0070] The content of the oligomer in the ink composition according to the third aspect of the present invention is about 1 to 50% by weight, preferably about 3 to 30% by weight.

#### Monomer

[0071] The ink composition according to the third aspect of the present invention contains a monomer. The term "monomer" used herein refers to a molecule which can constitute constituent units of the basic structure of a polymer. The monomer used in the ink composition according to the third aspect of the present invention is also called a "photopolymerizable monomer," and examples thereof include monofunctional acrylates and polyfunctional acrylates. According to a preferred embodiment of the present invention, the monomer may be the monomer having a tri- or higher functional reactive group described above in connection with the ink composition according to the first aspect of the present invention. This monomer has a structure of an acrylate of a low-molecular polyol and advantageously has low viscosity and can cure rapidly.

[0072] Preferred examples of monomers usable in the ink composition according to the third aspect of the present invention include diethylene glycol diacrylate, neopentyl glycol diacrylate, 1,6-hexanediol diacrylate, hydroxypiperic ester neopentyl glycol diacrylate, trimethylolpropane triacrylate, pentaerythritol triacrylate, dipentaerythritol hexaacrylate, acryloyl morpholine, 2-phenoxyethyl acrylate, (2,2,2-triacryloyloxymethyl)ethyl hydrogenphthalate, dipentaerythritol polyacrylate, and dipentaerythritol polyacrylate. Among them, acryloyl morpholine, 2-phenoxyethyl acrylate, (2,2,2-triacryloyloxymethyl)ethyl hydrogenphthalate, dipentaerythritol polyacrylate, and dipentaerythritol polyacrylate are more preferred.

[0073] The molecular weight of the monomer used in the ink composition according to the third aspect of the present



invention is about 100 to 3,000, preferably about 100 to 2,000.

[0074] The content of the monomer in the ink composition according to the third aspect of the present invention is about 1 to 70% by weight, preferably about 3 to 50% by weight.

[0075] The oligomer is copolymerized with a monomer to form a three-dimensional structure. Therefore, the content of the oligomer or the monomer in the ink composition according to the present invention should be determined by taking into consideration the polymerization efficiency, the polymerization speed, the resistance to shrinkage after polymerization, the polymer coating strength and the like.

#### Aqueous solvent and other ingredients

[0076] Aqueous solvents and other ingredients usable in the ink composition according to the third aspect of the present invention may be the same as those described above in connection with the ink composition according to the first aspect of the present invention. Preferred aqueous solvents and other ingredients may also be the same as those described above in connection with the ink composition according to the first aspect of the present invention. When the ink composition according to the third aspect of the present invention contains an aqueous solvent and other ingredients, the contents thereof may be the same as those described above in connection with the ink composition according to the first aspect of the present invention.

#### Ink jet recording method

[0077] The ink jet recording method according to one embodiment of the present invention comprises printing, on a recording medium, a photocurable ink composition for ink jet recording, comprising at least a colorant, a urethane oligomer, a monomer having a tri- or higher functional reactive group, a photopolymerization initiator, and an aqueous solvent.

[0078] The ink jet recording method according to this embodiment of the present invention, by virtue of the use of the photocurable ink composition for ink jet recording in printing, can realize good image quality and good prints.

[0079] The ink jet recording method according to another embodiment of the present invention comprises the steps of: forming droplets of a white ink composition for ink jet recording, comprising at least anatase titanium dioxide and an aqueous solvent; and depositing the droplets onto a recording medium to perform printing.

[0080] The ink jet recording method according to a further embodiment of the present invention comprises the steps of: forming droplets of a photocurable ink composition for ink jet recording, comprising at least anatase titanium dioxide, a photopolymerization initiator, an oligomer, a monomer, and an aqueous solvent; and depositing the droplets onto a recording medium to perform printing.

[0081] In the ink jet recording method according to the present invention, the ink composition is deposited on a recording medium followed by light irradiation. The applied light permits the photopolymerization initiator to produce radicals and the like which initiate a polymerization reaction of a oligomer (for example, a urethane oligomer) and a monomer (for example, a monomer having a tri- or higher functional reactive group), permitting a colorant (for example, anatase titanium dioxide) contained in the ink composition to be fixed onto the recording medium. It is considered that this can realize the formation of prints having high sharpness and excellent coating strength and chemical resistance even on the surface of media not penetrable by an aqueous medium, such as metals and plastics. The light irradiation may be visual light irradiation or ultraviolet irradiation with ultraviolet irradiation being particularly preferred.

[0082] According to a preferred embodiment of the present invention, when ultraviolet irradiation is used, the dose is not less than 100 mJ/cm<sup>2</sup>, preferably not less than 500 mJ/cm<sup>2</sup>, and not more than 10,000 mJ/cm<sup>2</sup>, preferably not more than 5,000 mJ/cm<sup>2</sup>. The dose of the ultraviolet light in the above range causes a satisfactory curing reaction. Further, the ultraviolet irradiation can advantageously prevent the fading of the colorant.

[0083] Lamps usable for the ultraviolet irradiation include metal halide lamps, xenon lamps, carbon arc lamps, chemical lamps, low-pressure mercury lamps, and high-pressure mercury lamps. For example, commercially available lamps, such as H lamp, D lamp, and v lamp manufactured by Fusion System, may be used.

[0084] Further, in the ink jet recording method according to the present invention, heating may be carried out simultaneously with or after the light irradiation. When the ink composition containing an aqueous solvent as an optional ingredient is deposited onto a recording medium, the removal of water remaining in the recording medium particularly by heating means can improve the efficiency of the polymerization reaction. This can enhance the fixation of prints on the recording medium and can improve the coating strength and the chemical strength of the prints.

[0085] Examples of methods usable for heating include a method wherein a heat source is brought into contact with the recording medium, and a method wherein the recording medium is heated without contact with a heat source, for example, a method wherein infrared radiation, microwave (electromagnetic radiation having a maximum wavelength at about 2,450 MHz) or the like is applied to the recording medium, or alternatively hot air is blown against the recording medium.

EXAMPLES

[0086] The present invention will be described in more detail with reference to the following examples, though it is not limited to these examples only.

Preparation of ink composition a		
Example 1a		
Aqueous dispersion of titanium oxide (pigment content 30% by weight)		33 wt%
Urethane oligomer (aqueous dispersion of urethane oligomer; NR-445, manufactured by Zeneca K.K.)		34 wt%
Monomer (dipentaerythritol polyacrylate, A-9530, manufactured by Shin-Nakamura chemical Co., Ltd.)		1.5 wt%
Photopolymerization initiator (Irgacure 1700, manufactured by Ciba Specialty Chemicals, K.K.)		1.5 wt%
Water		30 wt%
Example 2a		
Aqueous dispersion of titanium oxide (pigment content 30% by weight)		33 wt%
Urethane oligomer (aqueous dispersion of urethane oligomer; NR-445, manufactured by Zeneca K.K.)		26 wt%
Monomer (dipentaerythritol polyacrylate, A-9530, manufactured by Shin-Nakamura Chemical Co., Ltd.)		4.5 wt%
Photopolymerization initiator (Irgacure 1700, manufactured by Ciba Specialty Chemicals, K.K.)		1.5 wt%
Water		35 wt%
Example 3a		
Aqueous dispersion of titanium oxide (pigment content 30% by weight)		33 wt%
Urethane oligomer (aqueous dispersion of urethane oligomer; NR-445, manufactured by Zeneca K.K.)		19 wt%
Monomer (dipentaerythritol polyacrylate, A-9530, manufactured by Shin-Nakamura Chemical Co., Ltd.)		7.5 wt%
Photopolymerization initiator (Irgacure 1700, manufactured by Ciba Specialty Chemicals, K.K.)		1.5 wt%
Water		39 wt%
Example 4A		
Aqueous dispersion of carbon black (pigment content 30% by weight)		33 wt%
Urethane oligomer (aqueous dispersion of urethane oligomer; NR-445, manufactured by Zeneca K.K.)		26 wt%
Monomer (dipentaerythritol polyacrylate, A-9530, manufactured by Shin-Nakamura Chemical co., Ltd.)		4.5 wt%
Photopolymerization initiator (Irgacure 1700, manufactured by Ciba Specialty Chemicals, K.K.)		1.5 wt%
Water		35 wt%
Example 5a		
Aqueous dispersion of titanium oxide (pigment content 30% by weight)		33 wt%
Urethane oligomer (aqueous dispersion of urethane oligomer; NR-445, manufactured by Zeneca K.K.)		34 wt%
Monomer ( $\beta$ -methacryloyloxyethyl hydrogenphthalate; CB-1, manufactured by Shin-Nakamura Chemical Co., Ltd.)		1.5 wt%
Photopolymerization initiator (Irgacure 1700, manufactured by Ciba Specialty Chemicals, K.K.)		1.5 wt%
Water		30 wt%

Evaluation test a

[0087] Each of the ink compositions prepared in Examples 1a to 5a was loaded into a recording head of an ink jet recording apparatus, and then deposited on a print board as a recording medium to perform printing. Thereafter, the print was dried at 50 °C for 10 min, and the irradiated with ultraviolet light at a dose of 2,000 mJ/cm<sup>2</sup>.

[0088] The ink jet recording apparatus used was an ink jet printer MJ-510C (manufactured by Seiko Epson Corporation). A metal halide type irradiation lamp was used for the ultraviolet irradiation (wavelength 365 nm).

[0089] The ink compositions and the prints formed on the recording medium were evaluated by the following tests.

Evaluation 1a: Storage stability

[0090] The ink compositions were allowed to stand at 50°C for 10 days. Thereafter, 50% particle diameter in terms of volume (colorant) was measured, and evaluated.

[0091] Here, the "50% particle diameter in terms of volume" refers to such a diameter that, for the particle size distribution of a population of a colorant powder, corresponds to 50% of a cumulative curve on particle diameter prepared with the total volume of a population of the colorant powder being presumed to be 100%.

#### 5 Evaluation 2a: Pencil hardness

[0092] For the prints formed on the recording medium, the hardness was evaluated according to the method specified in JIS K 5400 (Hand Scratch Method in Pencil Scratch Test).

#### 10 Evaluation 3a: Chemical resistance

[0093] The prints formed on the recording medium were immersed in ethanol for 5 min. Thereafter, the prints were taken out of ethanol, and a toothbrush was reciprocated on each of the prints five times. The results were evaluated according to the following criteria.

15 [0094] A: The print was not separated at all from the recording medium.

[0095] B: The print was partially separated from the recording medium.

[0096] C: The print was entirely separated from the recording medium.

[0097] The ratio of the urethane oligomer to the monomer and the total content of the urethane oligomer and the monomer in the ink composition were as shown in Table 1 below. For the ink compositions prepared in Examples 1a to 5a, the results of the tests were as shown in Table 2 below.

Table 1

	Ratio		Total content, wt%
	Urethane oligomer	Monomer	Urethane oligomer + monomer
Ex. 1a	10	90	15
Ex. 2a	30	70	15
Ex. 3a	50	50	15
Ex. 4a	50	50	15
Ex. 5a	10	90	15

Table 2

	Evaluation 1a		Evaluation 2a	Evaluation 3a
	Initial $\mu\text{m}$	After standing $\mu\text{m}$		
Ex. 1a	0.18	0.22	3H	B
Ex. 2a	0.19	0.18	4H	A
Ex. 3a	0.19	0.20	4H	A
Ex. 4a	0.10	0.10	4H	A
Ex. 5a	0.18	1.21	F	C

#### 45 Preparation of ink composition b

##### Example 1b

Aqueous dispersion of anatase titanium dioxide (pigment content = 30% by weight, 50% particle diameter in terms of volume = 0.16 $\mu\text{m}$ )	33 wt%
Ethylene glycol	10 wt%
Water	57 wt%

##### Example 2b

Aqueous dispersion of anatase titanium dioxide (pigment content = 30% by weight, 50% particle diameter in terms of volume = 0.16 $\mu\text{m}$ )	33 wt%
Photopolymerization initiator (Irgacure 1700, manufactured by Ciba Specialty Chemicals, K.K.)	1.5 wt%
oligomer (aqueous dispersion of urethane oligomer; NR-445, manufactured by Zeneca K.K.)	34 wt%

(continued)

Preparation of ink composition b	
Example 2b	
Monomer (dipentaerythritol polyacrylate, A-9530, manufactured by Shin-Nakamura Chemical Co., Ltd.)	1.5 wt%
Ethylene glycol	5 wt%
Water	25 wt%
Example 3b	
Aqueous dispersion of rutile titanium dioxide (pigment content = 30% by weight, 50% particle diameter in terms of volume = 0.35 $\mu\text{m}$ )	33 wt%
Photopolymerization initiator (Irgacure 1700, manufactured by Ciba Specialty Chemicals, K.K.)	1.5 wt%
Oligomer (aqueous dispersion of urethane oligomer, NR-445, manufactured by Zeneca K.K.)	34 wt%
Monomer (dipentaerythritol polyacrylate, A-9530, manufactured by Shin-Nakamura Chemical Co., Ltd.)	1.5 wt%
Ethylene glycol	5 wt%
Water	25 wt%

Evaluation test b

[0098] Each of the ink compositions prepared in Examples 1b to 3b was loaded into a recording head of an ink jet recording apparatus, and then deposited on a print board as a recording medium to perform printing. Thereafter, the print was dried at 50 °C for 10 min, and then irradiated with ultraviolet light.

[0099] The ink jet recording apparatus used was an ink jet printer MJ-510C (manufactured by Seiko Epson Corporation). A metal halide type irradiation lamp was used for the ultraviolet irradiation (wavelength 365 nm).

[0100] The ink compositions and the prints formed on the recording medium were evaluated by the following tests.

Evaluation 1b: Dispersion stability

[0101] The ink compositions were allowed to stand at 50°C for 10 days, and then inspected for sediment.

Evaluation 2b: Pencil hardness

[0102] For the prints formed on the recording medium, the hardness was evaluated according to JIS K 5400 (Hand scratch Method in Pencil Scratch Test).

[0103] In this case, the ultraviolet irradiation were carried out on three dose levels of 1,000 mJ/cm<sup>2</sup>, 2,000 mJ/cm<sup>2</sup>, and 4,000 mJ/cm<sup>2</sup>.

Evaluation 3b: Printing stability

[0104] Each of the ink compositions was loaded into a recording head of an ink jet recording apparatus, and a pattern, in which characters and graphics intermingled, was printed on 200 sheets of papers of size A4 as a recording medium. At that time, the number of times of dropout was counted.

[0105] The type and particle diameter of titanium dioxide used in Examples 1b to 3b were as summarized in Table 3. For the ink compositions prepared in Examples 1b to 3b, the results of the tests were as summarized in Table 4.

Table 3

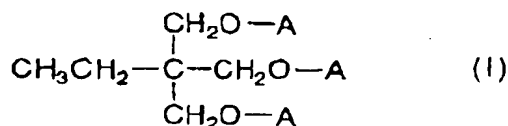
	Type of titanium dioxide	50% Particle diameter in terms of volume
Ex. 1b	Anatase titanium dioxide	0.16 $\mu\text{m}$
Ex. 2b	Anatase titanium dioxide	0.16 $\mu\text{m}$
Ex. 3b	Rutile titanium dioxide	0.35 $\mu\text{m}$

Table 4

	Evaluation 1b	Evaluation 2b			Evaluation 3b
	Sediment	Dose of ultraviolet light. mJ/cm <sup>2</sup>			Number of times of dropout
		1,000	2,000	4,000	
Ex. 1b	Absent				0
Ex. 2b	Absent	3H	4H	5H	2
Ex. 3b	Present	1H	2H	4H	35

## Claims

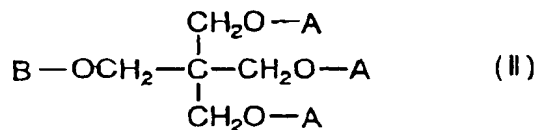
1. A photocurable ink composition for ink jet recording, comprising a colorant, a urethane oligomer, a monomer having a tri- or higher functional reactive group, a photopolymerization initiator, and an aqueous solvent.
2. The ink composition according to claim 1, which has a colorant content of 1 to 50% by weight.
3. The ink composition according to claim 1 or 2, wherein the colorant is anatase titanium dioxide.
4. The ink composition according to claim 3, wherein the anatase titanium dioxide has a particle diameter of not more than 0.2  $\mu\text{m}$ .
5. The ink composition according to any one of claims 1 to 4, which has a urethane oligomer content of 1 to 50% by weight.
6. The ink composition according to any one of claims 1 to 5, wherein the content of the monomer having a tri- or higher functional reactive group is 1 to 50% by weight.
7. The ink composition according to any one of claims 1 to 6, wherein the monomer having a tri- or higher functional reactive group is an acrylate monomer which has trimethylolpropane represented by formula (I) as a basic structure and at least three acryloyl groups:



wherein

A represents  $\text{CH}_2=\text{CHC}(\text{O})$  or  $\text{CH}_2=\text{CHC}(\text{O})\text{R}_n$  wherein R represents a straight-chain or branched alkoxy group having 1 to 5 carbon atoms and n represents the number of repetitions of R and is 1 to 10.

8. The ink composition according to any one of claims 1 to 6, wherein the monomer having a tri- or higher functional reactive group is an acrylate monomer which has pentaerythritol represented by formula (II) as a basic structure and at least three acryloyl groups:



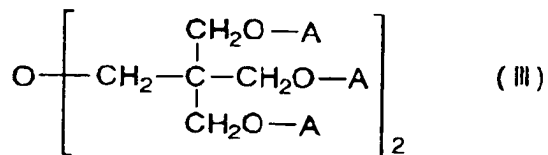
wherein

A represents H,  $\text{CH}_2=\text{CHC}(\text{O})$ , or  $\text{CH}_2=\text{CHC}(\text{O})\text{R}_n$  wherein R represents a straight-chain or branched alkoxy

group having 1 to 5 carbon atoms and n represents the number of repetitions of R and is 1 to 10; and B represents H, CH<sub>2</sub>=CHCO, or a higher acyl group having 1 to 5 carbon atoms,

provided that at least three out of all substituents of A and B comprise an acryloyl group.

9. The ink composition according to any one of claims 1 to 6, wherein the monomer having a tri- or higher functional reactive group is an acrylate monomer which has dipentaerythritol represented by formula (III) as a basic structure and at least three acryloyl groups:



wherein

A represents H, CH<sub>2</sub>=CHC(O), or CH<sub>2</sub>=CHC(O)R<sub>n</sub> wherein R represents a straight-chain or branched alkoxy group having 1 to 5 carbon atoms or a lactone having 1 to 5 carbon atoms and n represents the number of repetitions of R and is 1 to 10; and

B represents H, CH<sub>2</sub>=CHCO, or a higher acyl group having 1 to 5 carbon atoms,

provided that at least three out of all substituents of A comprise an acryloyl group.

10. A process for producing the ink composition according to any one of claims 1 to 9, comprising the steps of:

dissolving or dispersing a monomer having a tri- or higher functional reactive group in a urethane oligomer; and then adding a colorant, a photopolymerization initiator, and an aqueous solvent to the solution or the dispersion.

11. A white ink composition for ink jet recording, comprising at least anatase titanium dioxide and an aqueous solvent.

12. The ink composition according to claim 11, wherein the anatase titanium dioxide has a particle diameter of not more than 0.2 μm.

13. The ink composition according to claim 11 or 12, wherein the content of the anatase titanium dioxide is 1 to 50% by weight.

14. A photocurable white ink composition for ink jet recording, comprising anatase titanium dioxide, a photopolymerization initiator, an oligomer, a monomer, and an aqueous solvent.

15. The ink composition according to claim 14, wherein the anatase titanium dioxide has a particle diameter of not more than 0.2 μm.

16. The ink composition according to claim 14 or 15, wherein the content of the anatase titanium dioxide is 1 to 50% by weight.

17. The ink composition according to any one of claims 14 to 16, wherein the content of the oligomer is 1 to 50% by weight.

18. The ink composition according to any one of claims 14 to 17, wherein the content of the monomer is 1 to 70% by weight.

19. An ink jet recording method comprising the step of depositing droplets of an ink composition onto a recording medium to perform printing,

wherein the ink composition is one according to any one of claims 1 to 18.

20. The recording method according to claim 19, wherein a curing reaction is carried out after the deposition of the droplets of the ink composition onto the recording medium.

21. The recording method according to claim 20, wherein the curing reaction is carried out by ultraviolet irradiation.

22. The recording method according to claim 21, wherein the ultraviolet irradiation is carried out at a dose of 100 to 10,000 mJ/cm<sup>2</sup>.



European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number  
EP 00 30 2099

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	EP 0 337 705 A (SERICOL GROUP LTD) 18 October 1989 (1989-10-18) * page 2, line 41-55; example 1 *	1,2	C09D11/00
A	WO 97 31071 A (COATES BROTHERS PLC ;CAIGER NIGEL ANTONY (GB); SELMAN HARTLEY DAVI) 28 August 1997 (1997-08-28) * abstract *	1,14	
A	GB 2 303 376 A (FUJITSU ISOTEC LTD) 19 February 1997 (1997-02-19) * page 3, line 1 - page 4, line 33 *	2,4,5,7, 9,19-21	
A	EP 0 705 890 A (VIDEOJET SYSTEMS INT) 10 April 1996 (1996-04-10) * column 3, line 7-50 *	11-13	
A	EP 0 522 801 A (TDK CORP) 13 January 1993 (1993-01-13) * page 2, line 38-47 *	14	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
			C09D
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 13 June 2000	Examiner Miller, A
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone  Y : particularly relevant if combined with another document of the same category  A : technological background  O : non-written disclosure  P : intermediate document</p> <p>T : theory or principle underlying the invention  E : earlier patent document, but published on, or after the filing date  D : document cited in the application  L : document cited for other reasons  &amp; : member of the same patent family, corresponding document</p>			

EPO FORM 1500 (3/82) (P4/C01)



**ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.**

EP 00 30 2099

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.  
The members are as contained in the European Patent Office EDP file on  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

13-06-2000

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0337705	A	18-10-1989	GB 2217338 A	25-10-1989
WO 9731071	A	28-08-1997	AU 1804597 A	10-09-1997
			DE 69700697 D	02-12-1999
			DE 69700697 T	08-06-2000
			EP 0882104 A	09-12-1998
GB 2303376	A	19-02-1997	DE 19680301 T	07-05-1997
			WO 9628518 A	19-09-1996
EP 0705890	A	10-04-1996	JP 8113746 A	07-05-1996
EP 0522801	A	13-01-1993	DE 69202629 D	29-06-1995
			DE 69202629 T	21-09-1995
			JP 5085032 A	06-04-1993
			KR 9611718 B	30-08-1996
			US 5391685 A	21-02-1995

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

